Lecture 36. The Variation Principle

The variation theorem says that the expectation value of the energy for any wave function is equal to or greater than the ground state energy. This result provides a very powerful means of obtaining an upper bound on the true ground state energy. The proof is simple. Let $|i\rangle$ be a complete set of (unknown) energy eigenfunctions with eigenvalues $E_i$ ($i = 0, 1, 2,...$). Let $|a\rangle$ be some trial wave function that you are free to guess. So long as $|a\rangle$ has the correct boundary conditions, we can expand it in the energy basis:

$$|a\rangle = \sum_{i=0} c_i |i\rangle$$

Assuming that $|a\rangle$ is normalized, the expectation value of the energy is

$$\langle E \rangle = \langle a|H|a\rangle = \sum_i \sum_j c_i^* c_j \langle i|H|j\rangle = \sum_i \sum_j c_i^* c_j E_j \langle i|j\rangle = \sum_{i=0} |c_i|^2 E_i$$

Since $E_i \geq E_0,$

$$\langle E \rangle \geq \sum_{i=0} |c_i|^2 E_i = E_0$$

This result gives us a method for calculating an upper bound to the ground state energy: Simply guess $|a\rangle$ and calculate its energy. In the event that $|a\rangle$ is not normalized, we can do so on the spot:

$$\sum_i |c_i|^2 E_i \geq \int \frac{\psi_a^* H \psi_a}{\psi_a^* \psi_a} d\tau \geq E_0$$

Illustration: Solve for the ground state energy of the H atom with $l=0.$ Here and elsewhere we will use atomic units: $\hbar = m = e = 4\pi\varepsilon_0 = 1.$ In these units,

Bohr radius $= a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m e^2} = 1$

Ground state energy of H atom $= -\frac{1}{2} \frac{e^2}{4\pi\varepsilon_0 a_0} = -\frac{1}{2}$

In atomic units, the Hamiltonian for the hydrogen atom with $L=0$ is

$$H = -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{1}{r}$$

Let's try the wave function $\psi = e^{-r^2}$

Taking the appropriate derivatives,
\[
\frac{d\psi}{dr} = -2re^{-r^2}
\]
\[
\frac{d^2\psi}{dr^2} = -2e^{-r^2} - 4r^2e^{-r^2}
\]
we find
\[
H\psi = -2r^2e^{-r^2} + 3e^{-r^2} - \frac{1}{r}e^{-r^2}
\]
Evaluating the energy of this state,
\[
\langle E \rangle = \frac{\int_{0}^{\infty} \left( -2r^4e^{-2r^2} + 3r^2e^{-2r^2} - re^{-2r^2} \right) dr}{\int_{0}^{\infty} r^2e^{-2r^2} dr} = \left( \frac{-3}{8} + \frac{3}{4} \right) \frac{\pi}{8} - \frac{1}{4} \frac{\pi}{8} = \frac{3}{2} - \frac{2\sqrt{2\pi}}{\pi} = -0.096
\]
The correct value is \( E_{1s} = -\frac{1}{2} \).

Can we do better? Pick a better trial function. For example, \( \psi = e^{-\lambda^2} \). Repeating the calculation with \( \lambda \) as a constant, we get
\[
\langle E \rangle = \frac{3}{2} \lambda - 2\sqrt{\frac{2\lambda}{\pi}}
\]
Solving for the lowest possible value of the energy gives
\[
\frac{\partial \langle E \rangle}{\partial \lambda} = \frac{3}{2} - \frac{\sqrt{2}}{\sqrt{\pi\lambda}} = 0
\]
\[
\lambda = \frac{8}{9\pi}
\]
\[
E_{\min} = -\frac{4}{3\pi} = -0.424
\]
This is an example of the use of Gaussian functions to calculate energies and wave functions.

Another example is the He atom. To make sure that the Pauli Exclusion Principle is satisfied, we must use Slater determinants. For the two-electron case, the spin and spatial parts factor, and we needn’t worry about the spin when applying the Variation Principle. (See Levine Eq. (10.41).) The simplest possible trial wave function is the product of two hydrogenic functions. For the ground state of He we will use 1s functions,
\[
\psi_{1s}(r) = \sqrt{\frac{Z^3}{\pi}} e^{-Zr}
\]
The trial function is therefore
\[ \psi(r_1, r_2) = \psi_{1s}(r_1)\psi_{1s}(r_2) = \frac{Z^3}{\pi} e^{-r_1} e^{-r_2} \]

To allow for screening, we will replace \( Z = 2 \) with a free parameter, \( \lambda \), and the trial function for the entire atom (in atomic units) is
\[ \psi(r_1, r_2) = \frac{\lambda^3}{\pi} e^{-\lambda (r_1 + r_2)} \]

The Hamiltonian in atomic units is
\[ H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} = H_{01}(r_1) + H_{02}(r_2) + \frac{1}{r_{12}} \]

where \( Z \) is still equal to 2. (\( Z \) in the Hamiltonian is necessarily 2. The screening constant in the trial wave function is a variational parameter.) We have to calculate the matrix elements for each of the three terms on the right hand side. The first two terms are simply the ordinary hydrogen atom Hamiltonian for the individual electrons, but with screening constant of \( \lambda \).

Show that the expectation value for these two terms is
\[ \langle 1s(r_1)|H_{01}|1s(r_1)\rangle = \langle 1s(r_2)|H_{02}|1s(r_2)\rangle = \frac{\lambda^3}{2} - \lambda Z \]

In evaluating these quantities, you need to integrate over both \( r_1 \) and \( r_2 \). For example,
\[ \langle 1s(r_1)|H_{01}|1s(r_1)\rangle = \int_0^{\infty} \psi_{1s}(r_1)H_{01}(r_1)\psi_{1s}(r_1)r_1^2 dr_1 \int_0^{\infty} \psi_{1s}(r_2)^2 r_2^2 dr_2 \]

The third term is the repulsion energy of the two electrons. It can be evaluated analytically as a series of products of spherical harmonics. The result is
\[ \langle 1s(r_1)1s(r_2)|1s(r_1)1s(r_2)\rangle = \frac{5\lambda}{8} \]

Putting the pieces together, with \( Z = 2 \),
\[ \langle E \rangle = \lambda^2 - \frac{27}{8} \lambda \]
\[ \frac{d\langle E \rangle}{d\lambda} = 2\lambda - \frac{27}{8} = 0 \]
\[ \lambda = \frac{27}{16} \]

We see that there is significant screening. The minimum energy is \(-2.848 \text{ au}\), as compared with the true value of \(-2.9037\).
Lecture 37. The Linearized Variational Principle

One can do still better by assuming a more highly parameterized trial function. The cost in doing this is that the calculus becomes very messy. Is there an easier way? Choose a superposition of well-behaved functions, and let the variational parameters be coefficients of the superposition. In this case, all the equations are linear.

\[ \psi = \sum_{i=1}^{n} c_i |i\rangle. \]

We define the overlap integral

\[ S_{ij} = \langle i | j \rangle. \]

This integral need not necessarily be \( \delta_{ij} \), depending on the choice of functions. We similarly define the matrix elements

\[ H_{ij} = \langle i | H | j \rangle. \]

As before, we evaluate the expectation value of the energy, \( W \equiv \langle E \rangle \), expressed in terms of \( c_i, S_{ij}, \) and \( H_{ij} \):

\[ W = \sum_i \sum_j c_i^* c_j H_{ij} / \sum_i \sum_j c_i^* c_j S_{ij}. \]

We next solve for the minimum of \( W \) with respect to each of the \( c_i \). We end up with \( n \) linear equations for \( n+1 \) unknowns. For example, for the \( n=2 \) case,

\[ W = \frac{c_1^2 H_{11}^2 + c_1^* c_2 H_{12} + c_2^* c_1 H_{21} + c_2^2 H_{22}}{c_1^2 S_{11} + c_1^* c_2 S_{12} + c_2^* c_1 S_{21} + c_2^2 S_{22}} \]

\[ = \frac{N}{D} = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}. \]

We minimize \( W \) with respect to both \( c_1 \) and \( c_2 \). For \( c_1 \) we get

\[ \frac{\partial W}{\partial c_1} = \frac{D \frac{\partial N}{\partial c_1} - N \frac{\partial D}{\partial c_1}}{D^2} = 0 \]

\[ \frac{\partial N}{\partial c_1} = 2c_1 H_{11} + 2c_2 H_{12} \]

\[ \frac{\partial D}{\partial c_1} = 2c_1 S_{11} + 2c_2 S_{12} \]

The resulting equation is

\[ (H_{11} - WS_{11}) c_1 + (H_{12} - WS_{12}) c_2 = 0. \]
A similar equation comes from minimizing with respect to $c_2$:

$$(H_{21} - WS_{21})c_1 + (H_{22} - WS_{22})c_2 = 0$$

The solution for $W$ is obtained by getting the roots of a determinental equation:

$$\begin{vmatrix}
H_{11} - S_{11} & H_{12} - S_{12} & H_{13} - S_{13} \\
H_{21} - S_{21} & H_{22} - S_{22} & H_{23} - S_{23} \\
H_{31} - S_{31} & H_{32} - S_{32} & H_{33} - S_{33}
\end{vmatrix} = 0$$

$$(H_{11} - S_{11} W)(H_{22} - S_{22} W) - (H_{21} - S_{21} W)(H_{12} - S_{12} W) = 0$$

In general, for $n$ coefficients,

$$\begin{vmatrix}
H_{11} - S_{11} W & H_{12} - S_{12} W & H_{13} - S_{13} W \\
H_{21} - S_{21} W & H_{22} - S_{22} W & H_{23} - S_{23} W \\
H_{31} - S_{31} W & H_{32} - S_{32} W & H_{33} - S_{33} W \\
\vdots & \vdots & \vdots
\end{vmatrix} = 0$$

We solve for $n$ roots, which give the upper bounds to the $n$ lowest eigenvalues of $H$.

Once we have the roots, we can go back to the algebraic equations and solve for the $c_i$ coefficients. For example, in the $2x2$ problem, we have

$$c_2 = \frac{H_{11} - S_{11} W}{H_{21} - S_{21} W} c_1$$

$$c_1^2 + c_2^2 = 1$$

Application: The Stark effect in the H atom. The Hamiltonian, in atomic units, is

$$H = H_0 - Fr \cos \theta,$$

where $H_0$ is the Hamiltonian of the field-free Hamiltonian, and $F$ is the strength of the electric field. We will choose normalized eigenfunctions of $H_0$ as our variational functions, so that $S_{ij} = \delta_{ij}$. To be specific, we will take $n=2$, with

$$|1\rangle = |1s\rangle$$

$$|2\rangle = |2p_z\rangle$$

By straightforward integration, we get
\[
\begin{vmatrix}
H_{11} - W & H_{12} \\
H_{12} & H_{22} - W
\end{vmatrix} = \begin{vmatrix} -\frac{1}{2} - W & -2^{15/2} F / 3^5 \\
-2^{15/2} F / 3^5 & -\frac{5}{8} - W \end{vmatrix} = 0
\]

The result is a quadratic equation in \( W \), with the solution

\[
W_\pm = -\frac{5}{16} \pm \frac{3}{16} \sqrt{1 + \frac{2^{23}}{3^{12}} F^2}
\]

Recall that \( F \) is expressed in atomic units, so typically, \( F \ll 1 \). In that limit, the ground and excited state energies are

\[
W_\ominus = -\frac{1}{2} - \frac{2^{18}}{3^{11}} F^2 = E_{1s} - 1.4798 F^2
\]
\[
W_\oplus = -\frac{1}{8} + \frac{2^{18}}{3^{11}} F^2 = E_{2p} + 1.4798 F^2
\]

**Application to Molecules**

The simplest molecule is the \( H_2^+ \) ion. If we make the Born-Oppenheimer approximation, the Schrodinger equation may be solved analytically in spheroidal coordinates,

\[
\lambda = \frac{r_A + r_B}{R}
\]
\[
\mu = \frac{r_A - r_B}{R}
\]

In this coordinate system, the wave function is separable,

\[
\psi = L(\lambda)M(\mu)e^{im\phi}
\]

Note that the wave function is cylindrically symmetric and is an eigenfunction of \( \hat{L}_z \).

Although this problem can be solved exactly, it is useful to try the variational method. The simplest useful trial function allows the electron to reside on either nucleus. We will assume for this purpose a linear combination of atomic orbitals (LCAO), and for now will use only two orbitals:

\[
\psi = c_A \psi_{1s}(r_A) + c_B \psi_{1s}(r_B) = c_A |A\rangle + c_B |B\rangle
\]

We choose the individual orbitals to be orthonormal. This allows us to set \( S_{AB} = \delta_{AB} \), and the secular equation is
\[
\begin{vmatrix}
H_{AA} - W & H_{AB} - WS_{AB} \\
H_{AB} - WS_{AB} & H_{AA} - W
\end{vmatrix} = 0
\]

This equation reduces to
\[
H_{AA} - W = \pm (H_{AB} - ES_{AB})
\]
\[
W_\pm = \frac{H_{AA} \pm H_{AB}}{1 \pm S_{AB}}
\]

Within the Born-Oppenheimer approximation, the Hamiltonian is
\[
H = -\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}
\]

The first two terms are the ordinary Hydrogen Hamiltonian centered at nucleus A, which we denote as \(H_0\) with eigenvalue \(-1/2\). The last term is the internuclear repulsion, which is a constant at each fixed value of \(R\). We ignore it in the variational calculation and just add it at the end.

We can obtain by inspection the contributions to the matrix elements from \(H_0\):
\[
\langle A | H_0 | A \rangle = -\frac{1}{2}
\]
\[
\langle A | H_0 | B \rangle = -\frac{1}{2} S_{AB}
\]

The rest of the calculation is done using spheroidal coordinates. (This is not difficult). The result is
\[
S_{AB} = e^{-R} \left( 1 + R + \frac{R^2}{3} \right)
\]
\[
H_{AA} = -\frac{1}{2} - \frac{1}{R} \left[ 1 - e^{-2R} (1 + R) \right]
\]
\[
H_{AB} = -\frac{S_{AB}}{2} - e^{-R} (1 + R)
\]

Let’s look at the limiting behavior, ignoring the nuclear repulsion term:
\[
R \to \infty
\]
This is the result for a hydrogen atom.

\[ S_{AB} \to 0 \]
\[ H_{AA} \to -\frac{1}{2} \]
\[ H_{AB} \to 0 \]
\[ W_- \to -\frac{1}{2} \]

This is the result for a helium ion.

\[ R \to 0 \]
\[ S_{AB} \to 1 \]
\[ H_{AA} \to -\frac{1}{2} \]
\[ H_{AB} \to -\frac{3}{2} \]
\[ W_- \to -2 \]

The results at intermediate distances are shown in Chapter 13 of Levine (taken from Slater). We see that the ground state is bound, with a minimum near 2 au. The various figures show:

1. Electronic energy levels as a function of \( R \). At large \( R \) the levels become localized.
2. Electronic wave functions as a function of \( R \). These are molecular orbitals.
3. Potential energy curves with and without nuclear repulsion.

We can substitute the solutions for \( W \) back into the secular equation and obtain the LCAO coefficients. We find readily that \( c_A = \pm c_B \), and the normalization integral gives \( \sqrt{2(1 \pm S_{AB})} \). This leads to the two lowest molecular orbitals,

\[
\psi_{1\sigma_z}(r_A, r_B; R) = \frac{1}{\sqrt{2(1 + S_{AB})}} \{ \psi_{1s}(r_A) + \psi_{1s}(r_B) \}
\]

\[
\psi_{1\sigma_z}(r_A, r_B; R) = \frac{1}{\sqrt{2(1 - S_{AB})}} \{ \psi_{1s}(r_A) - \psi_{1s}(r_B) \}
\]

We can demonstrate the normalization as follows:

\[
\int |\psi_{1s}(r_A) \pm \psi_{1s}(r_B)|^2 d\tau = \int |\psi_{1s}(r_A)|^2 d\tau + \int |\psi_{1s}(r_B)|^2 d\tau + 2\int |\psi_{1s}(r_A)\psi_{1s}(r_B)| d\tau = 2 + S_{AB}
\]

The wave functions have two types of symmetry:

1. Axial symmetry, with quantum number \( m = 0, 1, 2, \ldots \) corresponding to \( \sigma, \pi, \delta, \ldots \) states.
2. Inversion symmetry, corresponding to \( g \) and \( u \) states.
A completely different approach is to partition the Hamiltonian into a zero-order part, $\hat{H}_0$, which has known eigenfunctions and eigenvalues, and a small perturbation, $\hat{H}'$. We introduce a perturbation parameter, $\lambda$, such that

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}'.$$

The eigenfunctions and eigenvalues are

$$\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \equiv E_n^{(0)} |n\rangle$$

$$\hat{H} \psi_n = E_n \psi_n$$

We next expand $\psi_n$ and $E_n$ in Taylor series in $\lambda$:

$$\psi_n(x, \lambda) = (\psi_n^{(0)})_{\lambda=0} + \left( \frac{\partial \psi_n^{(0)}}{\partial \lambda} \right)_{\lambda=0} \lambda + \frac{1}{2} \left( \frac{\partial^2 \psi_n^{(0)}}{\partial \lambda^2} \right)_{\lambda=0} \lambda^2 = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots$$

$$E_n(\lambda) = (E_n^{(0)})_{\lambda=0} + \left( \frac{\partial E_n^{(0)}}{\partial \lambda} \right)_{\lambda=0} \lambda + \frac{1}{2} \left( \frac{\partial^2 E_n^{(0)}}{\partial \lambda^2} \right)_{\lambda=0} \lambda^2 = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$

We substitute both of these equations into the Schrödinger equation,

$$(\hat{H}_0 + \lambda \hat{H}')(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots) \psi_n + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots)$$

Next, we equate terms of equal powers of $\lambda$. The result is a series of correction terms for $\psi_n$ and $E_n$, evaluated in the limit of $\lambda \rightarrow 1$. In the special case that $E_n$ is not degenerate,

$$\lambda^0: \quad \hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$$

$$\lambda^1: \quad \hat{H}_0 \psi_n^{(1)} + \hat{H}' \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)}$$

$$\lambda^2: \quad \hat{H}_0 \psi_n^{(2)} + \hat{H}' \psi_n^{(1)} = E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)}$$

Next, we multiply on the left by $\psi_m^{(0)}$ and integrate. The first equation is just the unperturbed Schrödinger equation. For $m=n$, the second equation gives

$$E_n^{(1)} = \langle n | \hat{H}' | n \rangle \equiv H_n^{(1)}$$

For $m \neq n$, the second and third equations give

$$E_n^{(2)} = \sum_{m \neq n} \frac{|H_n^{(mn)}|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{H_n^{(mn)}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$
Obtaining these last two results requires expanding \( \psi_m^{(1)} \) in the unperturbed basis. The coefficient for \( m = n \) is chosen to be zero. This is allowed because we can choose to absorb this component of \( \psi_m^{(1)} \) in \( \psi_m^{(0)} \). Levine calls this “intermediate normalization”:
\[
1 = \langle n^{(0)} | n \rangle = \langle n^{(0)} | n^{(0)} \rangle + \lambda \langle n^{(0)} | n^{(1)} \rangle + \lambda_2 \langle n^{(0)} | n^{(2)} \rangle + \ldots
\]

For \( \lambda \neq 0 \), all the coefficients \( a_n^{(x=0)} = 0 \).

We illustrate these results with a problem that we can solve exactly, namely the 2x2 Hamiltonian. Previously we found that
\[
\lambda = \frac{1}{2} (H_{11} + H_{22}) \pm \frac{1}{2} \left[ (H_{11} - H_{22})^2 + 4\varepsilon^2 \right]^{1/2} = \frac{1}{2} (H_{11} + H_{22}) \pm \frac{1}{2} (H_{11} - H_{22}) \sqrt{1 + \frac{4\varepsilon^2}{(H_{11} - H_{22})^2}},
\]
where \( \varepsilon = H_{12} \) is not necessarily a small number. If we do choose \( \varepsilon \ll |H_{11} - H_{22}| \) we get:
\[
\lambda_+ \approx H_{11} + \frac{\varepsilon^2}{H_{11} - H_{22}} = H_{11} - \frac{\varepsilon^2}{H_{22} - H_{11}}
\]
\[
\lambda_- \approx H_{22} - \frac{\varepsilon^2}{H_{11} - H_{22}} = H_{22} + \frac{\varepsilon^2}{H_{22} - H_{11}}
\]

We see that the result for the ground state is identical to that obtained with second order perturbation theory:
\[
E_1 = E_1^{(0)} + E_1^{(1)} + E_1^{(2)} = H_{11} + H_{11}' + \frac{(H_{12}')^2}{H_{11}' - H_{22}'}
\]

(In comparing the two results, note that in setting up the exact problem we absorbed the diagonal terms of the perturbation into the unperturbed Hamiltonian. Also, there is only one term in the sum because there are only two basis states.)

The equivalence extends to the wave functions as well. For the original 2x2 result, we found that
\[
\psi_+ \approx \psi_0 + \frac{\varepsilon}{H_{11} - H_{22}} \psi_1
\]
\[
\psi_- \approx \psi_1 - \frac{\varepsilon}{H_{11} - H_{22}} \psi_0
\]
These eigenfunctions are orthogonal to first order in \( \varepsilon \). They are also identical to the result of first order perturbation theory.
Lecture 39. Perturbation Theory: The Anharmonic Oscillator

\[
\hat{H}_0 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2
\]

\[
\hat{H}' = cx^3 + dx^4
\]

We must be careful here because \(\hat{H}'\) contains both a first order and a second order term. Here by “order” we mean the size of the perturbation. Both first order and second order perturbation theory may be applied to each of these terms. First order perturbation theory gives \(\langle n|x^3|n\rangle = 0\) and \(\langle n|x^4|n\rangle \neq 0\). To stop at first order, however, as does Levine, is erroneous because the second order perturbation term for \(x^3\) is comparable in magnitude to the first order correction for \(x^4\). Levine gets the wrong sign for the anharmonicity by ignoring the \(x^3\) part of the potential. Writing the perturbation in reduced units,

\[
\hat{H}' = c\alpha^3 y^3 + d\alpha^3 y^4 = c'y^3 + d'y^4,
\]

and expressing the energy in units of \(\hbar\nu\), we can expand the energy of the ground state to first order in \(y^4\) and second order in \(y^3\). There are only two terms in the second order summation.

\[
E = \frac{1}{2} + d'\langle 0|y^4|0\rangle - c'^2 \sum_{s=1}^{\infty} \frac{1}{s} \left|\langle 0|y^3|s\rangle\right|^2
\]

\[
= \frac{1}{2} + d'\langle 0|y^4|0\rangle - c'^2 \left\{ \left|\langle 0|y^3|1\rangle\right|^2 + \frac{1}{3} \left|\langle 0|y^3|3\rangle\right|^2 \right\}
\]

where

\[
\psi_s(y) = \frac{1}{\sqrt{s!2^s \pi^{1/2}}} H_s(y)e^{-y^2/2}.
\]

We worked out the matrix elements earlier in the course. Their numerical values are

\[
\langle 0|y^4|0\rangle = \frac{3}{4}
\]

\[
\langle 0|y^3|1\rangle = \frac{3}{4} \sqrt{2}
\]

\[
\langle 0|y^3|3\rangle = \frac{\sqrt{3}}{2}
\]

Putting the pieces together, we find

\[
E = \frac{1}{2} + \frac{3}{4} d' - \frac{11}{8} c'^2
\]

To relate this to actual molecules, we need to know the coefficients \(c\) and \(d\). A useful approach is to start with the Morse potential, which is an empirical function.
\[ V(x) = D_x \left( 1 - e^{-\gamma x} \right)^2 = D_x \left( 1 - 2e^{-\gamma x} + e^{-2\gamma x} \right) \]

Expanding in a Taylor series,

\[ V(x) = D_x \left[ 1 - 2 \left( 1 - \gamma x + \frac{1}{2} \gamma^2 x^2 - \frac{1}{6} \gamma^3 x^3 + \frac{1}{24} \gamma^4 x^4 + \ldots \right) \right] + \left( 1 - 2\gamma x + 2\gamma^2 x^2 - \frac{4}{3} \gamma^3 x^3 + \frac{2}{3} \gamma^4 x^4 + \ldots \right) \]

\[ = D_x \gamma^2 x^2 - D_x \gamma^3 x^3 + \frac{7}{12} D_x \gamma^4 x^4 + \ldots \]

The quadratic term gives us the force constant,

\[ D_x \gamma^2 x^2 = \frac{1}{2} k x^2 \]

or

\[ k = 2 D_x \gamma^2. \]

Introducing dimensionless variables,

\[ y = x / \alpha \]

\[ \alpha = \sqrt{\hbar \omega / k} \]

we can express the coefficients in the potential as

\[ D_x \gamma^3 \alpha^3 = \left( D_x \gamma^2 \right) y \frac{\hbar \omega}{k} \sqrt{\frac{\hbar \omega}{k}} = \frac{1}{2} k y \frac{\hbar \omega}{k} \sqrt{\frac{\hbar \omega}{k}} = \frac{1}{2} \sqrt{8} \frac{\hbar \omega}{D_x} \]

\[ D_x \gamma^4 \alpha^4 = \frac{1}{D_x} \frac{k^2}{4} \left( \frac{\hbar \omega}{k} \right)^2 = \frac{1}{4} \left( \frac{\hbar \omega}{D_x} \right) \frac{\hbar \omega}{k} \]

Defining a dimensionless parameter,

\[ \eta = \frac{\hbar \omega}{D_x}, \]

we can write the dimensionless potential as

\[ \frac{V(x)}{\hbar \omega} = \frac{1}{2} y^2 + \sqrt{\frac{\eta}{8}} y^3 + \frac{7}{48} \eta y^4. \]

This result gives us \( c' \) and \( d' \), allowing us to determine the energy,

\[ \frac{E}{\hbar \omega} = \frac{1}{2} + \frac{7}{64} \eta - \frac{11}{64} \eta^2 = \frac{1}{2} - \frac{11}{64} \eta. \]
This result agrees perfectly with the exact answer given in Herzberg for the Morse oscillator (Spectra of Diatomic Molecules, p 101), expressed in wave numbers,

\[ G(v) = \frac{1}{2} \omega_e \left( v + \frac{1}{2} \right)^2 - \omega_e x_e \left( v + \frac{1}{2} \right)^2 \]

where

\[ x_e = \frac{\hbar \omega_e}{4D_e}. \]

For \( v=0 \), we get the result derived above.

It is instructive to compare this with the result from linearized variational theory. We truncate the potential at \( y^3 \) and include only two states in the trial wave function,

\[ \psi = c_0 \phi_0 + c_1 \phi_1 \]

The matrix elements needed in the secular equation are

\[ H_{00} = \frac{1}{2} \]
\[ H_{11} = \frac{3}{2} \]
\[ H_{10} = H_{01} = -\frac{1}{\sqrt{8}} \sqrt{\eta} \langle 0 | y^3 | 3 \rangle = -\frac{3}{8} \sqrt{\eta}. \]

The secular equation then is

\[
\begin{vmatrix}
\frac{1}{2} - W & H_{01} \\
H_{01} & \frac{3}{2} - W
\end{vmatrix} = 0
\]

Expanding the determinant, we get

\[ W = 1 \pm \frac{1}{2} \sqrt{1 + 4H_{01}^2}. \]

Taking the lower value and expanding the square root,

\[ W \approx 1 - \frac{1}{2} \left( 1 + 2H_{01}^2 \right) = \frac{1}{2} - H_{01}^2 = \frac{1}{2} = \frac{9}{64} \eta. \]

The correction term has the correct sign but is approximately a factor of 2 too large.
Another example is the He atom. For the ground state,

\[ \hat{H}_0(r_1, r_2) = \hat{H}_0(r_1) + \hat{H}_0(r_2) \]

\[ \hat{H}'(r_1, r_2) = \frac{1}{r_{12}} \]

\[ \psi_1^{(0)}(r_1, r_2) = \left( \frac{Z^3}{\pi} \right) e^{-Z(r_1 + r_2)} \]

\[ E_1^{(0)} = -\frac{Z^2}{2} - \frac{Z^2}{2} = -Z^2 \]

\[ E_1^{(1)} = \frac{5Z}{8} \]

\[ E_1^{(0)} + E_1^{(1)} = -2.75 \text{au} \]

where \( Z = 2 \). The variation method does a better job than first order perturbation theory.

The Stark effect is a bit trickier. The first order Stark correction for the 1s state is zero. To evaluate the first order Stark effect for \( n = 2 \) requires dealing with a 4-fold degeneracy. The answer is first order in \( F \). The second order Stark effect for 1s corresponds to an induced dipole.

\[ E_n^{(2)} = \sum_{m \neq n} \frac{|H_{nm}^\prime|^2}{E_n^{(0)} - E_m^{(0)}} \]

The first term in this series is produced by the 2p state, with a value

\[ E_1^{(2)} \approx \left| (1s|F \cos \theta|2p_z) \right|^2 = \left( \frac{2^{15}}{3^{10}} \right) F^2 = -\frac{2^{18}}{3^{11}} F^2 \]

This is identical to the result of variation method without adjustable parameters.

**Lecture 40. Degenerate Perturbation Theory**

Suppose we have \( N \) states with unperturbed energies \( E_1^{(0)}, E_2^{(0)}, ..., E_N^{(0)} \), and that two of those states, say \( \alpha \) and \( \beta \), have equal energies. How does this degeneracy affect the energies in the presence of a perturbation, \( H' \)? To see this, let’s review the unperturbed case to first order.

\[ \hat{H} = \hat{H}_0 + \lambda H' \]

\[ \psi = \psi^{(0)} + \lambda \psi^{(1)} \]

\[ E = E^{(0)} + \lambda E^{(1)} \]
for any state \( n \). Substituting into Schrodinger’s equation gives to first order in \( \lambda \),

\[
(\hat{H}_0 + \lambda \hat{H}^\prime)(\psi_n^{(0)} + \lambda \psi_n^{(1)}) = (E_n^{(0)} + \lambda E_n^{(1)})(\psi_n^{(0)} + \lambda \psi_n^{(1)})
\]

\[
(\hat{H}_0 - E_n^{(0)})\psi_n^{(1)} = (E_n^{(1)} - \hat{H}^\prime)\psi_n^{(0)}.
\]

Next, we expand \( \psi_n^{(1)} \) in the unperturbed (zeroth order) basis set,

\[
\psi_n^{(1)} = \sum_{s=1}^{N} a_{ns}^{(1)} \psi_s^{(0)}, \quad a_{nn}^{(1)} = 0
\]

giving

\[
\sum_{s=1}^{N} a_{ns}^{(1)} (\hat{H}_0 - E_n^{(0)}) \psi_s^{(0)} = (E_n^{(1)} - \hat{H}^\prime) \psi_n^{(0)}
\]

Left multiply by \( \psi_n^{(0)*} \) and integrating, the LHS vanishes, and the RHS becomes

\[
E_n^{(1)} - \langle n|H^\prime|n \rangle = 0
\]

or

\[
E_n^{(1)} = H_{nn}^\prime.
\]

Now let’s repeat this for the degenerate case, where two levels, \( \alpha \) and \( \beta \), have the same energy. The main difference is that for the degenerate levels we have to take a linear combination of the zero-order states to obtain the correct limit when \( \lambda \to 0 \).

\[
\psi_n^{(0)} = a_{n\alpha}^{(0)} \psi_\alpha^{(0)} + a_{n\beta}^{(0)} \psi_\beta^{(0)}.
\]

We get for the expansion of the first order correction to the wave function:

\[
\psi_n^{(1)} = a_{n\alpha}^{(1)} \psi_\alpha^{(0)} + a_{n\beta}^{(1)} \psi_\beta^{(0)} + \sum_{s=\alpha, \beta} a_{ns}^{(1)} \psi_n^{(0)}.
\]

Substituting both expansions into \( (\hat{H}_0 - E_n^{(0)})\psi_n^{(1)} = (E_n^{(1)} - \hat{H}^\prime)\psi_n^{(0)} \) gives:

\[
(\hat{H}_0 - E_n^{(0)})\left(a_{n\alpha}^{(1)} \psi_\alpha^{(0)} + a_{n\beta}^{(1)} \psi_\beta^{(0)}\right) + \sum_{s=\alpha, \beta} a_{ns}^{(1)} (E_s^{(0)} - E_n^{(0)}) \psi_s^{(0)} = (E_n^{(1)} - \hat{H}^\prime)\left(a_{n\alpha}^{(1)} \psi_\alpha^{(0)} + a_{n\beta}^{(1)} \psi_\beta^{(0)}\right)
\]

The first term on the left hand side vanishes. We can make the second term on the LHS also vanish by left multiplying by \( \psi_\alpha^{(0)*} \) or \( \psi_\beta^{(0)*} \) and integrating:

\[
\psi_\alpha^{(0)*} \text{ gives: } 0 = a_{n\alpha}^{(1)} E_n^{(1)} - a_{n\alpha}^{(1)} H_{\alpha\alpha}^\prime - a_{n\alpha}^{(1)} H_{\alpha\beta}^\prime
\]

\[
\psi_\beta^{(0)*} \text{ gives: } 0 = a_{n\beta}^{(1)} E_n^{(1)} - a_{n\alpha}^{(1)} H_{\beta\alpha}^\prime - a_{n\beta}^{(1)} H_{\beta\beta}^\prime
\]
The three unknowns (energy and two coefficients), leads to a secular equation:

\[
\begin{vmatrix}
H'_{\alpha\alpha} - E^{(1)}_n & H'_{\alpha\beta} \\
H'_{\beta\alpha} & H'_{\beta\beta} - E^{(1)}_n
\end{vmatrix} = 0.
\]

Solve for the eigenvalues and eigenvector coefficients in the usual manner. Possible generalizations: Higher order degeneracy and higher order perturbations.

What are the eigenfunctions? In the state expansion of \( \psi_n^{(1)} \), the coefficients \( a^{(1)}_{n\alpha} \) and \( a^{(1)}_{n\beta} \) are zero because of “intermediate normalization” defined by Levine. This simply means that these terms are absorbed into the zero order wave function. The equation

\[
(H_0 - E^{(0)}_n)\psi^{(1)}_n = (E^{(1)}_n - H')\psi^{(0)}_n
\]

is

\[
\sum_{s=\alpha,\beta} a^{(1)}_{ns}(E^{(0)}_s - E^{(0)}_n)\psi^{(0)}_s = (E^{(1)}_n - H')\left(a^{(0)}_{n\alpha}\psi^{(0)}_\alpha + a^{(0)}_{n\beta}\psi^{(0)}_\beta\right)
\]

Left multiply by \( \psi^{(0)*}_k \) and integrating,

\[
(E^{(0)}_k - E^{(0)}_n)a^{(1)}_k = -H'_{ka}a^{(0)}_{n\alpha} - H'_{kb}a^{(0)}_{n\beta}
\]

\[
a^{(1)}_{nk} = \frac{H'_{ka}a^{(0)}_{n\alpha} + H'_{kb}a^{(0)}_{n\beta}}{(E^{(0)}_n - E^{(0)}_k)}
\]

Where \( k \neq \alpha,\beta \). Only one term survives on the LHS because \( \langle k | s \rangle = \delta_{ks} \). The \( E^{(1)}_n \) term vanishes on the RHS for the same reason.

What are the properties of the eigenvalues? The secular determinant gives

\[
E^{(1)}_\pm = \frac{1}{2}\left\{(H'_{\alpha\alpha} + H'_{\beta\beta}) \pm \sqrt{(H'_{\alpha\alpha} - H'_{\beta\beta})^2 + 4H'^2_{\alpha\beta}}\right\}
\]

Assuming that

\[
H'_{\alpha\beta} \ll |H'_{\alpha\alpha} - H'_{\beta\beta}|
\]

We can expand the square root and get

\[
E^{(1)}_+ = H'_{\alpha\alpha} + \frac{H'^2_{\alpha\beta}}{H'_{\alpha\alpha} - H'_{\beta\beta}}
\]

\[
E^{(1)}_- = H'_{\beta\beta} + \frac{H'^2_{\alpha\beta}}{H'_{\alpha\alpha} - H'_{\beta\beta}}
\]
where
\[ H'_{\alpha\alpha} > H'_{\beta\beta}. \]

Compare this result with non-degenerate perturbation theory, where
\[ E^{(1)}_n = H'_{\alpha\alpha}, H'_{\beta\beta} \]

Here the levels repel each other.

**Lecture 41. The Stark Effect**

The perturbation produced by an electric field of strength \( F \) is
\[ H' = -Fr \cos \theta. \]

The first order Stark correction for the 1s state is zero because the wave function does not have \( z \)-symmetry. To evaluate the first order Stark effect for \( n = 2 \) requires dealing with a 4-fold degeneracy. The answer is first order in \( F \). We show this as follows:

Noting that \( \hat{H}', \hat{L}_z = 0 \), we choose as our basis set
\[ \psi_1 = 2s, \psi_2 = 2p_0 \propto \cos \theta, \psi_3 = 2p_1 \propto \sin \theta, \psi_4 = 2p_{-1} \propto \sin \theta. \]

We need to calculate all the matrix elements of \( \hat{H}' = -Fr \cos \theta \). We first show that the diagonal elements are all zero.

\[ |1\rangle: \int_0^\pi \cos \theta \sin \theta d\theta = \int_0^1 x dx = 0 \]

\[ |2\rangle: \int_0^\pi \cos^3 \theta \sin \theta d\theta = \int_0^1 x^3 dx = 0 \]

\[ |3\rangle, |4\rangle: \int_0^\pi \sin^2 \theta \cos \theta \sin \theta d\theta = \int_0^1 (1-x^2) x dx = 0 \]

The only non-zero element is \( \langle 2s | H' | 2p_0 \rangle \propto \int_0^\pi \cos^2 \theta \sin \theta d\theta = \int_0^1 x^2 dx = \frac{2}{3} \)

\[ \psi_{2s} = \frac{1}{4 \sqrt{2\pi}} a_0^{-5/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0} \]

\[ \psi_{2p_0} = \frac{1}{4 \sqrt{2\pi}} a_0^{-5/2} r e^{-r/2a_0} \]
\[ \langle 2s | H' | 2p_0 \rangle = -F \left[ \frac{1}{4\sqrt{2\pi}} a_0^{5/2} \right]^2 \cdot 2\pi \cdot 2 \int_0^r \left( 2 - \frac{r}{a_0} \right) e^{-r/a_0} dr = -3Fa_0 \]

The secular equation is:

\[
\begin{pmatrix}
-W & -3Fa_0 & 0 & 0 \\
-3Fa_0 & -W & 0 & 0 \\
0 & 0 & -W & 0 \\
0 & 0 & 0 & -W \\
\end{pmatrix} = 0.
\]

\[ W^2 \left( W^2 - 9e^2 F^2 a_0^2 \right) = 0 \]

The roots are 0, 0, 3Fa_0, -3Fa_0. The splitting of 6Fa_0/\hbar c is 2.6 cm^{-1} for F = 10^6 V/cm.

The surviving degeneracy in first order comes from 2p_z, which is a consequence of the axial symmetry of the perturbation.

The degeneracy is lifted only for 2s and 2p_0, with wave functions

\[ |\pm\rangle = \frac{1}{\sqrt{2}} \left( |l = 0, m = 0\rangle \pm |l = 1, m = 0\rangle \right) \]

Returning to the 1s state of hydrogen, the second order, non-degenerate Stark effect is caused by an induced dipole.

\[ E^{(2)}_n = \sum_{mn} \frac{|H'_{mn}|^2}{E^{(0)}_n - E^{(0)}_m} \]

The first term in this series is produced by the 2p_z state, with a value

\[ E^{(2)}_{1s} \approx \left( \frac{1}{3} \frac{F_1}{3} \right) F^2 = \left( \frac{2}{3} \frac{15}{10} \right) F^2 = \left( \frac{2}{3} \right)^2 F^2 \]

This is identical to the result of linearized variational treatment of H(1s), where we considered only the 1s and 2p_0 states.